Universality and Critical Behavior at the Mott transition

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We report conductivity measurements of Cr-doped V_2O_3 using a variable pressure technique. The critical behavior of the conductivity near the Mott-insulator to metal critical endpoint is investigated in detail as a function of pressure and temperature. The critical exponents are determined, as well as the scaling function associated with the equation of state. The universal properties of a liquid-gas transition are found. This is potentially a generic description of the Mott critical endpoint in correlated electron materials.

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Since the early recognition by Mott [1, 2] that electron-electron interactions are responsible for the insulating character of many transition-metal oxides, extensive research over the last decade has demonstrated the key importance of this phenomenon for the physics of strongly correlated electron materials. Outstanding examples [3] are superconducting cuprates, manganites displaying colossal magnetoresistance, or fullerene compounds. There are two routes for achieving a metallic state, starting from a Mott insulating material. The first is to introduce charge carriers by doping. The second, closely connected to Mott's original ideas, is to reduce the ratio U/W between the typical strength of local Coulomb repulsion (U) and the typical kinetic energy of the relevant electrons (W). This can be achieved in practice, in some materials, by selected atomic substitutions or by applying pressure. The most widely studied example [4, 5, 6, 7, 8] is Cr-doped Vanadium sesquioxide $(V_{1-x}\ Cr_x)_2O_3$ which displays a transition from a paramagnetic Mott insulator to a strongly correlated metal. The transition into the metallic state can be triggered by lowering temperature (at sufficiently small chromium concentration x), by decreasing x or by increasing pressure P (early studies[4, 5, 6, 7] have revealed that decreasing concentration by $\Delta x \sim -0.01$ corresponds to an applied

pressure of $\Delta P \sim 4$kbar). The transition is first-order, with a significant reduction of the lattice spacing through the insulator-to-metal transition, indicating a coupling between electronic and lattice degrees of freedom. The first-order transition line in the (P, T) - or (x, T) -phase diagram ends in a second-order critical endpoint (P_c, T_c).

We report on transport experiments which allow for a precise identification of the critical behavior associated with this critical endpoint, a question of fundamental importance in understanding the Mott transition. Recent theoretical developments have proposed a description of the critical behavior in simplified purely electronic models (and also of the crossovers between distinct transport regimes close to the critical point). Despite extensive studies of this material, the critical behavior has not been elucidated so far experimentally. The key technique used in

the present work is to perform conductivity measurements as a function of continuously varying pressure, at constant temperature (see ref. [5] for an early study). This is particularly well adapted to the present situation in which the transition line in the (T, P) plane is very sharp. In contrast, the work of Kuwamoto *et al.*[8] investigated conductivity as a function of temperature for a discrete set of chromium concentrations x.

We use an isopentane liquid pressure cell, and control the value of pressure with an accuracy of 1 bar. Conductivity is measured at constant regulated temperature with an accuracy of order 0.1 K, as a function of pressure, using a standard four-probe method. All our measurements were performed on crystals of $(V_{0.989}\ Cr_{0.011})_2O_3$ grown using the skull-melter technique followed by appropriate annealing [9]. The choice of a Cr concentration $x = 0.011$ is such that the sample is on the insulating side of the transition at ambient pressure but that a moderate pressure (a few kilobars) drives the system into the metallic state (or, alternatively, a decrease in temperature). This is visible on the data set (Fig. 1A), which displays the conductivity σ as a function of pressure P, for several temperatures in the range $290\text{K} < T < 485\text{K}$. These data are obtained by decreasing pressure from $P = 6$ kbar down to ambient pressure, going from a high-conductivity metallic regime to a low-conductivity insulating regime. For temperatures smaller than the critical temperature T_c this transition is discontinuous, with a sudden jump of the conductivity. In order to locate precisely this critical point and to demonstrate the first-order nature of the transition, we have performed hysteresis experiments in which the conductivity is measured during increasing and decreasing pressure sweeps at a slow rate of order 25 bar/min (Fig. 1A). From the difference between the measured conductivities in these two sweeps (Fig. S2), two characteristic pressures can be identified, $P_M(T)$ and $P_I(T)$ ($P_M < P_I$), corresponding respectively to the lowest pressure at which a metallic state can be sustained while decreasing pressure (P_M), and to the highest pressure at which an insulating state can be sustained while increasing pressure (P_I). These two spinodal lines , plotted as a function of temperature on Fig.

1B, merge at the critical endpoint (P_c, T_c). We can then estimate: $P_c \simeq 3738$ bar, $T_c \simeq 457.5$ K. Varying pressure rather than temperature is essential for a precise determination of T_c, which is compatible with the early estimate ($\simeq 450$K) by Kuwamoto et al.[8]. At the critical temperature, the pressure dependence of $\sigma(P, T_c)$ becomes singular, with a vertical tangent at the critical pressure $P = P_c$ (Fig. 2A). For $T > T_c$, this singular behavior is replaced by a continuous variation of the conductivity with pressure, which nevertheless defines a sharp crossover line in the (P, T) phase diagram (as also depicted in Fig. 1B). This crossover line extrapolates to a temperature of order ~ 500K for the pressure (~ 5kbar) corresponding to the pure V_2O_3 compound. Interestingly, the location of this crossover coincides with the one detected in early NMR experiments[10].

We now show that the critical singularities found in the vicinity of the critical endpoint (P_c, T_c) can be analyzed in the framework of the scaling theory of the liquid-gas transition of classical systems[11]. The analogy between the latter and the finite-temperature Mott transition has been emphasized early on by Castellani *et al.*[12] (see also Ref. [5]). The insulating phase (in which the Vanadium is mainly in the V^{3+} state, corresponding to the d^2 configuration) can be pictured as a "gas" phase with a low density of double occupancies or holes (corresponding to V^{2+} and V^{4+}, or d^3 and d^1, respectively). The metallic phase corresponds to a "liquid" with a sizeable density of holes and double occupancies. Recently, this analogy has been given firm theoretical foundations within the framework of a Landau theory[13, 14] derived from dynamical mean-field theory (DMFT)[15]. In this framework, a scalar order parameter ϕ is associated with the low-energy electronic degrees of freedom which build up the quasiparticle resonance in the strongly correlated metallic phase close to the transition. This order parameter couples to the singular part of the double occupancy (hence providing a connection to the picture described above), as well as to other observables such as the Drude weight or dc-conductivity. Because of the scalar nature of the order parameter, the transition falls in the Ising universality

class. Coupling to lattice degrees of freedom can also be included in the theory[16] without changing this conclusion. In the following we denote by r the scaling variable corresponding to the temperature scaling axis in the Ising model analysis (i.e. to the term $r\phi^2$ in the Landau functional) and by h the scaling axis corresponding to magnetic field (i.e. to the symmetry-breaking term $-h\phi$). These scaling variables are a priori linear combinations of $(T-T_c)/T_c$ and $(P-P_c)/P_c$. However, our data are compatible with no or little mixing, so that we choose in all the following: $r=(T-T_c)/T_c+\cdots$, $h=(P-P_c)/P_c+\cdots$ (the dots indicate higher order terms). Denoting by $\sigma_c=\sigma(P_c,T_c)$ ($\simeq 449.5\ \Omega^{-1}$cm^{-1}) the measured conductivity at the critical point, it is expected that $\sigma(P,T)-\sigma_c$ depends linearly on the order parameter $\langle\phi\rangle$ close to the critical point. (This can be explicitly proven in the context of DMFT). At $T=T_c$, this implies a critical singularity of the form: $\sigma(P,T_c)-\sigma_c\sim h^{1/\delta}$ with δ the critical exponent associated with the singular dependence of the magnetization at the critical point in the Ising model. The data in Fig. 2A are very well fitted by this form, as demonstrated in the inset. Over more than two decades in $h\propto(P-P_c)/P_c$, we find the best-fit value of the exponent to be $\delta\simeq 3$, i.e. the mean-field value. In a narrow pressure interval ($\Delta P\simeq 10$ bar) close to the critical pressure, indication for a crossover towards a value $\delta\simeq 5$ is found, close to the three-dimensional (3D) Ising value $\delta\simeq 4.814$.

We now address the critical behavior away from T_c by studying the temperature dependence of the conductivity in the following manner. For $T<T_c$, we focus on the conductivity of the metallic state, at the high-pressure boundary of the coexistence region. That is, we consider $\sigma^*(T)\equiv\sigma_{met}(P_I(T),T)-\sigma_c$ with $P_I(T)$ the spinodal of the insulating phase. This quantity, plotted in Fig. 2B, is expected to display the critical behavior of the order parameter, by analogy with the liquid-gas transition: $\sigma^*(T)\sim(-r)^\beta$ with $r\propto(T-T_c)/T_c$. As shown in the inset (Fig. 2B), a mean-field value of the critical exponent $\beta\simeq 0.5$ is found to fit the data over almost two decades away from the critical point. In a narrow temperature interval $\Delta T\simeq 4$K

close to T_c ($\Delta T/T_c \simeq 0.01$), some indication for a crossover towards a non mean-field value $\beta \simeq 0.34$ is found, close to the 3D Ising value $\beta \simeq 0.327$. We also consider the derivative of the conductivity with respect to pressure, in the metallic state, taken on the same spinodal line: $\chi(T) \equiv (d\sigma_{met}(P,T)/dP)|_{P=P_I(T)}$. This quantity can be defined as well for $T > T_c$ by taking the derivative at the inflection point of the $\sigma(P)$ curve (Fig. 1A). Following the liquid-gas analogy, it corresponds to the magnetic susceptibility in the equivalent Ising model: $\chi \propto d\langle\phi\rangle/dh$. As shown in Fig. 2C, it is found to diverge as $\chi \sim \chi_+/(T-T_c)^\gamma$ for $T > T_c$ and as $\chi \sim \chi_-/(T_c-T)^{\gamma'}$ for $T < T_c$. The exponent γ, as well as the (universal) amplitude ratio χ_+/χ_-, are found to be close to their mean-field values: $\gamma = \gamma' = 1$, $\chi_+/\chi_- = 2$. Very close to T_c, the noise in the numerical derivative involved in the determination of χ prevents a reliable determination of deviations from mean-field, in contrast to the above study of the conductivity itself.

Finally, we demonstrate that the whole set of conductivity data in the metallic phase can be scaled onto a universal form, which can be written as:

$$\sigma_{met}(P,T) - \sigma_c = (\delta h)^{1/\delta}\, f_\pm\left(\frac{\delta h}{|r|^{\gamma\delta/(\delta-1)}}\right) \qquad (1)$$

In this expression, $\delta h = h - h_I$ denotes the difference between the "field" $h = (P-P_c)/P_c$ and its value on the spinodal line of the insulating phase $h_I = (P_I - P_c)/P_c$, i.e.: $\delta h = (P - P_I(T))/P_c$. This amounts to a simple shift of the field variable on the standard form [11] of the universal equation of states near a liquid-gas critical point. The functions f_+ and f_- are universal scaling functions which apply for $T > T_c$ ($r > 0$) and $T < T_c$ ($r < 0$), respectively. When written in this form, the equation of state is such that the order parameter $\sigma^*(T)$ defined above is recovered when the limit $\delta h \to 0$ is taken in the right-hand side of Eq. 1. The pressure-dependent data sets for many different temperatures have been plotted in this manner (Fig. 3), in which the two exponents γ and δ were taken as adjustable parameters (Fig. S3) in order to

obtain the best collapse of all the data points onto single curves. This leads to values of these exponents close to the mean-field ones $\gamma \simeq 1, \delta \simeq 3$, which provides a strong check on the individual determination of each critical exponent performed above. The quality of the scaling is seen to be excellent over a very large range of variation of the scaling variables (several decades). It is apparent that the scaling functions obey the expected asymptotic behaviors: $f_+(x \ll 1) \sim x^{1-1/\delta}$, $f_-(x \ll 1) \sim x^{-1/\delta}$ and $f_\pm(x \gg 1) \sim$ const.. This finding is essential to ensure that Eq. 1 be compatible with the critical behavior of the order parameter σ^* at small and large field, for both $T < T_c$ and $T > T_c$, investigated previously in Fig. 2. It also implies that the critical exponents obey the relation $\gamma = \beta(\delta - 1)$, in agreement with the above determination of β.

These universal scaling properties of the pressure- and temperature-dependent conductivity experimentally demonstrate that the electronic degrees of freedom undergo a liquid-gas phase transition at the Mott critical endpoint. Critical exponents and a universal scaling function have been determined. Our results are consistent with mean-field values over most of the parameter range, with some indication for three-dimensional Ising behavior very close to the transition. A possible explanation for why the range of validity of mean-field theory is so large can be put forward by analogy with the theory of conventional superconductors. There, the key point is the existence of a very large length scale (the pair coherence length), much larger than the lattice spacing (or the Fermi wavelength). Here, the Mott insulator can be thought of as a state in which holes and doubly occupied sites form bound states due to their Coulomb interaction. The spatial extension ξ of these bound states is related to their energy (the Mott gap Δ) by $\Delta \sim h^2/(2m\xi^2)$. Given the measured value of Δ in samples close to the transition, this leads to the conclusion that ξ is indeed a large length-scale, of order a few nanometers. Finally, we emphasize that our results provide experimental support to the early idea of Ref. [12] and to recent theories of the Mott critical endpoint based on the dynamical mean-field (DMFT) approach[13, 14, 15]. While

further effort should be devoted to the inclusion of lattice degrees of freedom in these theories, simplified treatments of these effects[16] do emphasize the key role of electronic degrees of freedom in the transition.

References and Notes

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Figure captions

Fig. 1A: Conductivity as a function of decreasing pressure, for temperatures ranging from $T = 485$K ($> T_c = 457.5$K, orange curves) down to $T = 290$K ($< T_c$, blue curves). The dark yellow curve is the conductivity at T_c. Only a selected set of values of T has been displayed, for clarity. (For a two-dimensional plot of the data, see Fig. S1) Examples of an hysteresis cycle are shown for $T = 290$K and $T = 348$K. For a plot of the difference of conductivities measured in decreasing and increasing pressure sweeps, see Fig. S2.

Fig. 1B: Phase diagram of Cr-doped Vanadium Sesquioxide V_{1-x} $Cr_x)_2O_3$ as a function of pressure and temperature, in the range $1\text{bar} < P < 6\text{kbar}$ and $290\text{K} < T < 500\text{K}$ investigated in this work. At a given temperature T, the metallic state can be obtained for pressures higher than the spinodal pressure $P_M(T)$, and the insulating state for pressures lower than the spinodal pressure $P_I(T)$. These two spinodal lines delimit a pressure range $P_M < P < P_I$ in which the two states coexist (hatched region on the figure). This coexistence region closes at the critical endpoint (P_c, T_c) ($P_c \simeq 3738\text{bar}, T_c \simeq 457.5\text{K}$). The crossover line above this point (dashed) corresponds to the inflection point in the $\sigma(P)$ curves.

Fig. 1C: Schematic global phase diagram of Cr-doped Vanadium Sesquioxide V_{1-x} $Cr_x)_2O_3$ as a function of pressure and temperature, deduced from Ref. [7].

Fig.2 These plots demonstrate how the critical exponents δ, β and γ can be inferred from the study of the conductivity and of its derivative with respect to pressure (see text).

Fig. 2A: At the critical temperature $T = T_c$, the conductivity σ is plotted as a function of pressure. The (plain) red line is a fit to $\sigma - \sigma_c \sim (P - P_c)^{1/\delta}$, with $\delta = 3$. The use of a logarithmic scale (inset) confirms this value, and also reveals a non mean-field regime for P close to P_c.

Fig. 2B: Order parameter $\sigma^*(T) = \sigma(P_I(T), T) - \sigma_c$ *vs.* T/T_c, for $T < T_c$. The line is a fit to

$(T_c - T)^\beta$ with $\beta = 0.5$. The inset (logarithmic scale) reveals a non mean-field regime close to T_c.

Fig. 2C: Derivative of the conductivity (analogous to a susceptibility χ, as described in text), for $T < T_c$ and $T > T_c$. The plain lines are fits to $\chi_\pm |T - T_c|^{-\gamma}$, with $\gamma = 1$ and $\chi_+/\chi_- = 2$.

Fig. 3: Scaling plot of the conductivity onto a universal equation of state. The whole data set in the metallic state has been used in order to plot $(\sigma - \sigma_c)/(P - P_I)^{1/\delta}$ *vs.* $(P - P_I)/(T - T_c)^{\gamma\delta/(\delta-1)}$, as described in the text. The data collapse onto two universal curves for $T > T_c$ and $T < T_c$, corresponding to the universal scaling functions $f_\pm$ in Eq.(1).

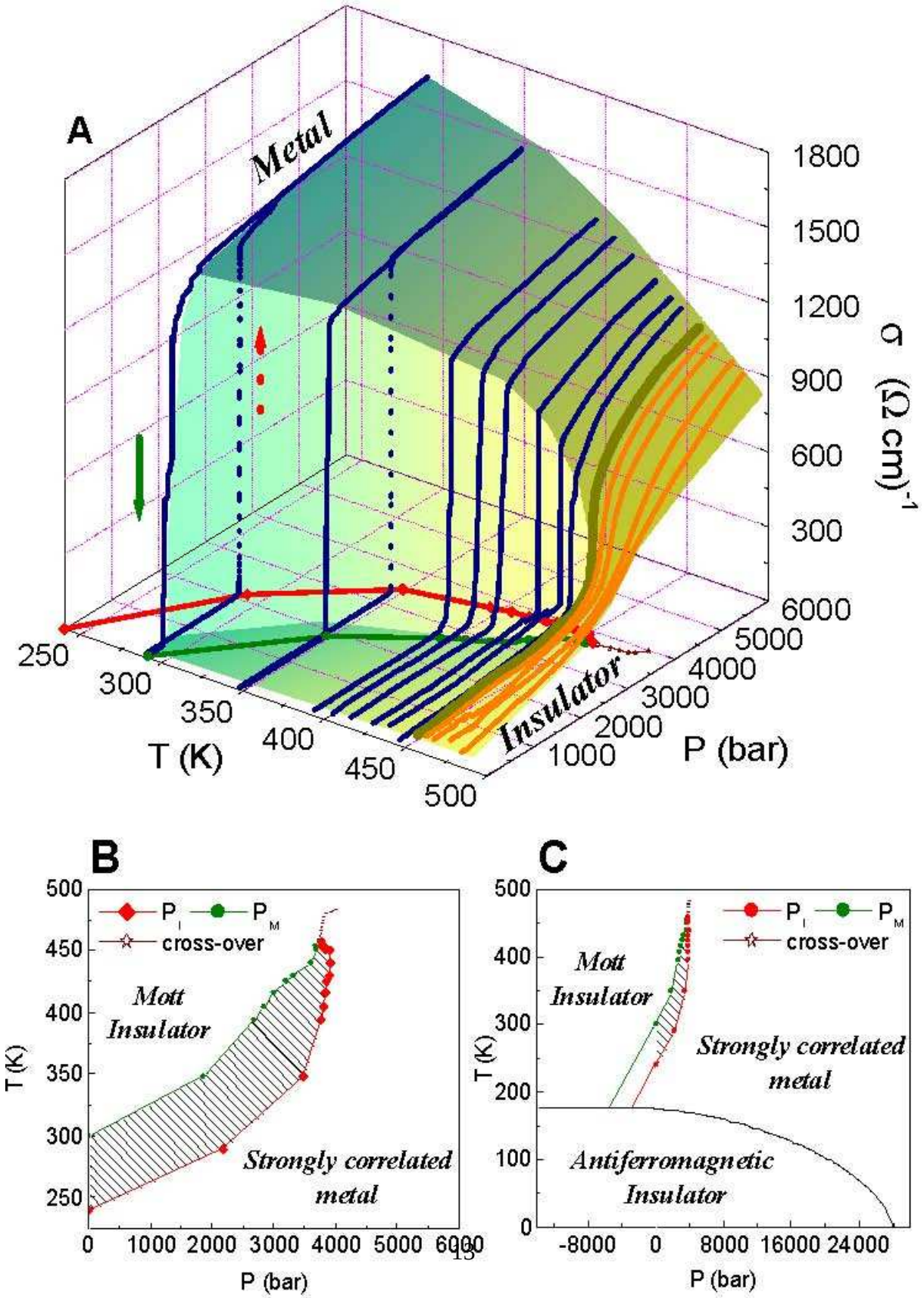
A
Metal
Insulator
T (K)
P (bar)
ρ (Ω cm)-1
250
300
350
400
450
500
1000
2000
3000
4000
5000
6000
300
600
900
1200
1500
1800
B
C
P_I
P_M
cross-over
Mott Insulator
Strongly correlated metal
Antiferromagnetic Insulator
T (K)
P (bar)

Figure 1:

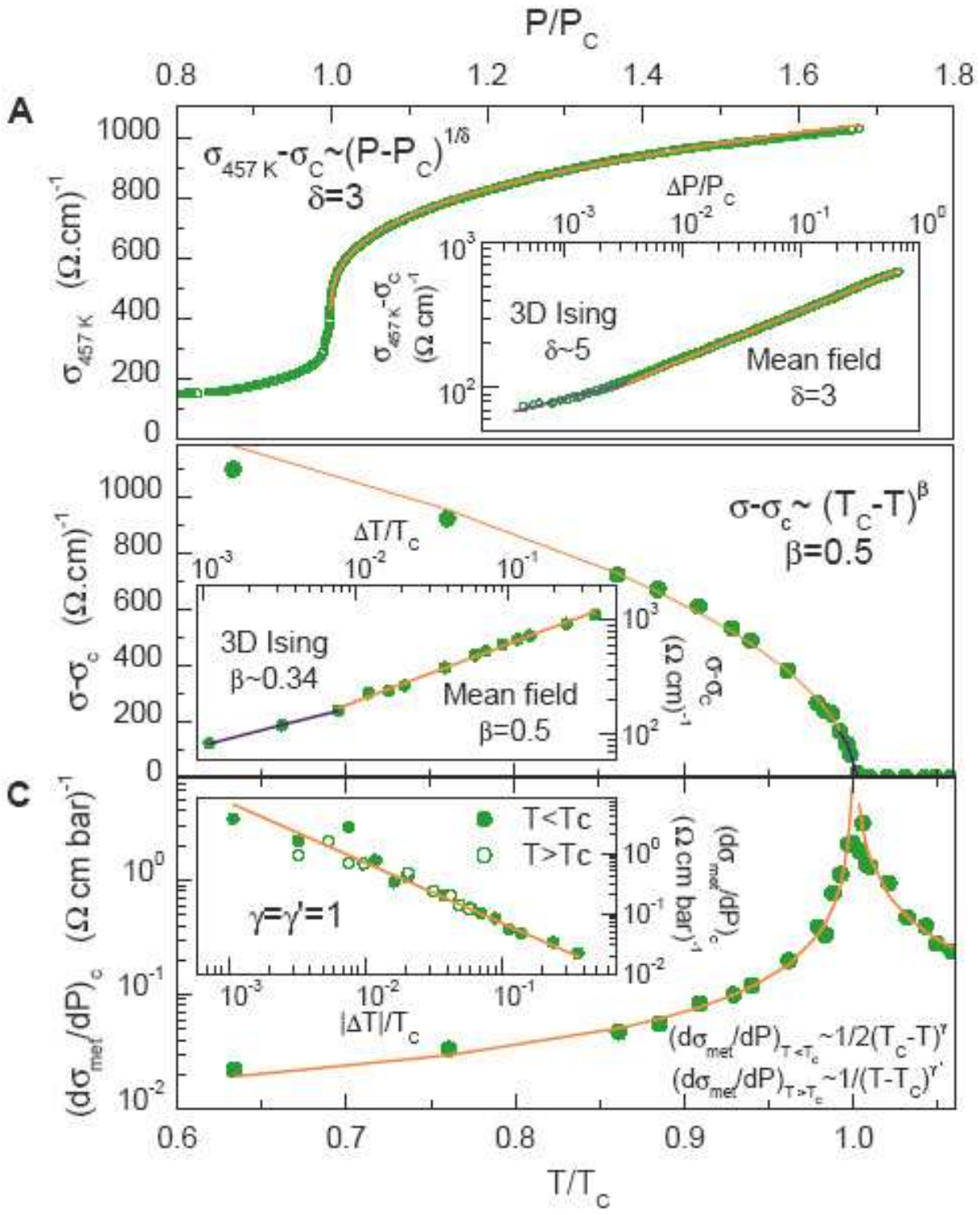
P/P_C
A
σ_457 K-σ_C~(P-P_C)^1/δ
δ=3
σ_457 K (Ω.cm)^-1
ΔP/P_C
3D Ising
δ~5
Mean field
δ=3
σ-σ_c~(T_C-T)^β
β=0.5
σ-σ_c (Ω.cm)^-1
ΔT/T_C
3D Ising
β~0.34
Mean field
β=0.5
C
(dσ_met/dP)_c (Ω cm bar)^-1
T<Tc
T>Tc
γ=γ'=1
|ΔT|/T_C
(dσ_met/dP)_T<Tc~1/2(T_C-T)^γ
(dσ_met/dP)_T>Tc~1/(T-T_C)^γ'
T/T_C

Figure 2:

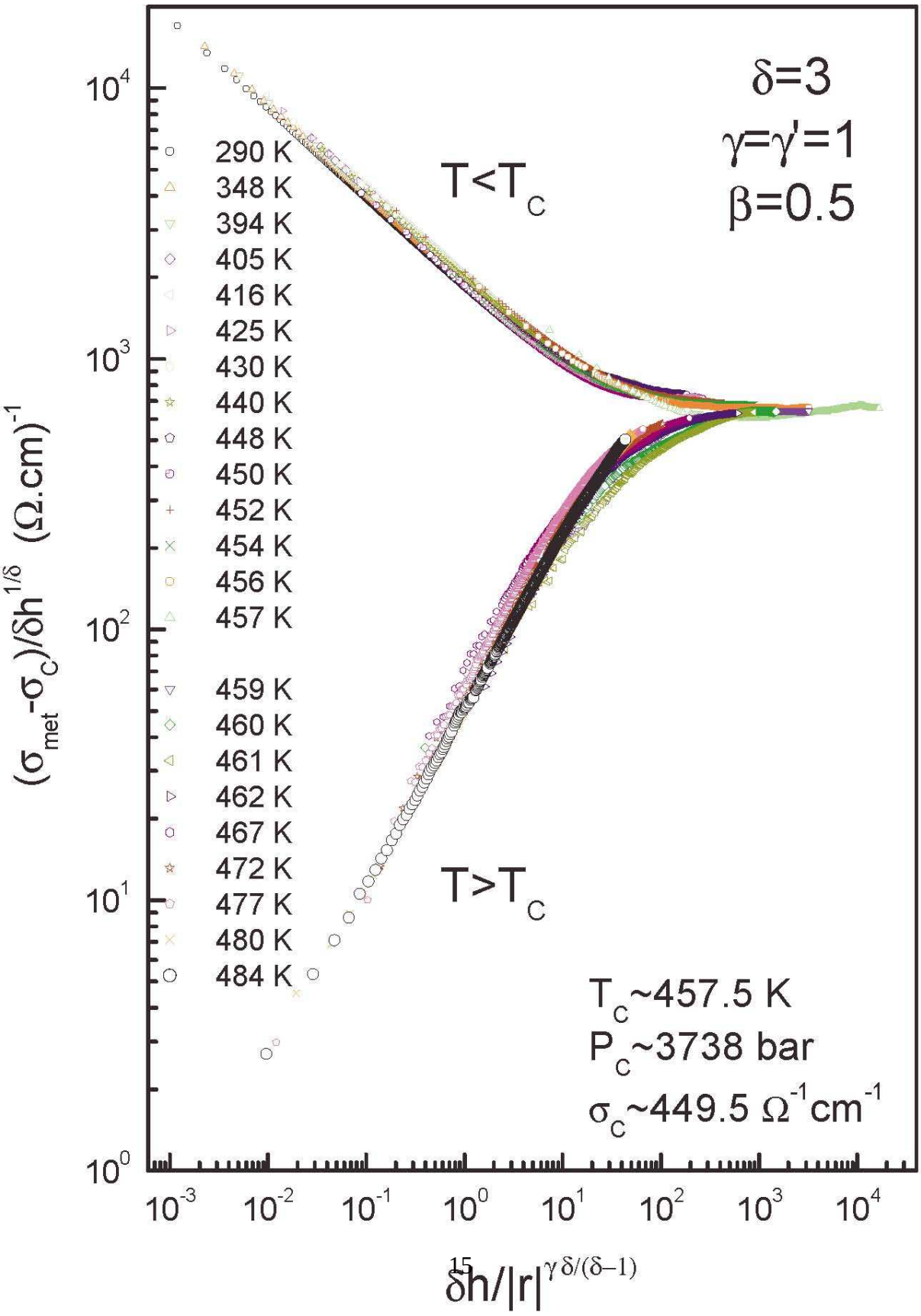
δ=3
γ=γ'=1
β=0.5
T<T_C
T>T_C
290 K
348 K
394 K
405 K
416 K
425 K
430 K
440 K
448 K
450 K
452 K
454 K
456 K
457 K
459 K
460 K
461 K
462 K
467 K
472 K
477 K
480 K
484 K
T_C~457.5 K
P_C~3738 bar
σ_C~449.5 Ω^-1cm^-1
(σ_met-σ_C)/δh^1/δ (Ω.cm)^-1
δh/|r|^γδ/(δ–1)

Figure 3: